United States Patent

[11] 3,617,476

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[21] Appl. No. **815,233**
[22] Filed **Apr. 10, 1969**
[45] Patented **Nov. 2, 1971**

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[54] **LUBRICATING OIL PROCESSING**
10 Claims, No Drawings

[52] **U.S. Cl.** **208/36,**
208/18, 208/80, 208/96, 208/143
[51] **Int. Cl.** **C10g 43/08**
[50] **Field of Search** 208/18, 80,
108, 36, 309, 96, 143

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ABSTRACT: Lubricating oils of high-viscosity index are produced in good yield by a sequence involving mild hydrogenation, solvent refining and dewaxing. The process is particularly effective for the treatment of lube oil fractions containing at least 1 percent Conradson Carbon Residue using N-methyl pyrrolidone as the solvent.

LUBRICATING OIL PROCESSING

This invention is concerned with the treatment of lubricating oil stocks. More particularly, it is concerned with a novel processing scheme whereby lubricating oil stocks are converted in good yields into high quality lubricating oils.

Various procedures are available for the refining of lubricating oils. For example solvent refining is used to remove low VI aromatic compounds and reactive impurities by contacting the oil with a solvent which preferentially dissolves aromatic compounds. As a substitute for solvent refining, it has been proposed to subject the lubricating oil stock to relatively severe catalytic hydrotreating conditions for the saturation of aromatic compounds. This generally carried out at a pressure between about 1,000 and 2,000 p.s.i.g. Another step in the refining of the lube oil stocks is solvent dewaxing for the removal of high-melting point wax and correspondingly a reduction in the pour point of the oil. This is accomplished by adding a preferential solvent for the oil, chilling and filtering. Clay contacting has been employed to remove color clay bodies from the oil to produce an oil of improved color. Color improvement can also be effected by mild hydrogenation, for example, at a relatively low temperature and pressure as distinguished from the hydrogen treatment for aromatic saturation to improve the viscosity index.

In conventional lube oil refining the solvent extraction step is carried out first to recover about 45–75 percent of the charge as refined oil and to reject about 25–55 percent of the charge as dark colored viscous extract. Since the extract amounts to a relatively large percentage of the charge and is not suitable for upgrading by dewaxing and either clay contacting or mild hydrogenation to a satisfactory quality level for use as a lube oil, solvent extraction has, up to the present, been the most logical and economical process to apply first.

The refiner then has the option of removing color bodies from the oil by mild hydrogenation or clay treating and then reducing the pour point of the oil by solvent dewaxing or by following the solvent refining with solvent dewaxing and then with clay contacting or mild hydrogenation. The choice between these two sequences is usually made on the basis of which one is the most practical for a given refinery. For example, if a finished refined wax is to be produced dewaxing may be chosen ahead of mild hydrogenation to permit separate treatment of the wax. Different conditions would then be used on the dewaxed oil than would be used if the hydrogenation were to precede the solvent dewaxing in which case wax would be present in the charge to the hydrogenation reactor.

It is an object of the present invention to provide a novel sequence for the treatment of the lube oil stocks to increase the yield of high quality lubricating oils. Another object is to produce lubricating oils of improved properties such as viscosity index and color. Another object is to reduce the amount of solvent necessary for the solvent refining of a particular lubricating oil. These and other objects will be obvious to those skilled in the art from the following disclosure.

According to my process, a lubricating oil stock is first subjected to mild hydrogenation, the hydrogenation product is then solvent refined and the solvent refined material is then dewaxed. I have found that by the process of my invention yields of refined oil obtained in the solvent refining step are in the range of about 10–20 percent higher by volume basis charge to the extraction zone when refining to the same quality level than when no mild hydrogenation precedes the solvent refining. In addition, as compared to raw stocks the mildly hydrogenated stocks have higher API gravities, lower refractive indexes and higher viscosity indexes. My novel process also permits reduction in the severity of the solvent extraction conditions whereby refining solvent dosages can be reduced when charging the mildly hydrogenated stocks. This means that in existing units the capacity can be increased or, in units to be built, smaller units can handle the desired throughput.

The process of my invention may be applied to any lubricating oil stock such as a distillate obtained by the vacuum distillation of crude petroleum or by the deasphalting of a vacuum residuum. Sources of lubricating oil stocks which may be processed according to the invention are West Texas crude, Louisiana crude, Coastal crude and the like. It is an unexpected feature of my invention that the mild hydrogenation conditions result in increased solvent refining response not only in light "clean" stocks but also in relatively dirty stocks containing at least 1percent Conradson Carbon such as deasphalted residuum. In addition, the combination of mild hydrogenation with N-methyl pyrrolidone as the solvent results in products of good color, even when the stock contains more than 1 percent Conradson Carbon.

The first step in my process is a mild hydrogenation. It is to be distinguished from the severe hydrorefining used as a substitute for solvent extraction for the saturation of aromatics to improve the VI of the lubricating oil. The mild hydrogenation conditions include a pressure not greater than 600 p.s.i.g, preferably 300–500 p.s.i.g. Temperatures may range from about 575° to about 800° F., preferred range being 575°–650° F. Hydrogen is introduced into the reaction zone at a rate of 300–5,000 or more s.c.f.b. (standard cubic feet per barrel of charge), a preferred rate being from 500–2,000 s.c.f.b. Space velocities (volumes of oil per volume of catalyst per hour) may range from about 0.2–3, preferably from 0.5–1.5.

The catalyst used in the mild hydrogenation step comprises a hydrogenating component advantageously carried on an inert support. Suitable hydrogenating components comprise Group VIII metals or their compounds such as the oxides or sulfides or mixtures thereof. Examples of Group VIII metals are iron, nickel, cobalt, platinum and palladium. Advantageously the Group VIII metal or compound is used in conjunction with the Group VI metal such as molybdenum, tungsten or chromium or compounds thereof. The catalyst support suitably comprises a refractory inorganic oxide material such as silica, alumina, magnesia, titania or mixtures thereof. The support should be relatively inert and have little if any activity at reaction conditions.

Particularly suitable catalysts are those containing from 2–8 percent cobalt or nickel and 5–20 percent molybdenum or 2–10 percent nickel and 10–30 percent tungsten by weight of the total catalyst composite supported on alumina. Due to the mildness of the hydrogenating conditions, the liquid yield of product is essentially 100 percent that of the charge.

The mildly hydrogenated oil is then subjected to solvent refining with a solvent having an affinity for aromatic hydrocarbons which is at most only partially soluble in the oil so that two phases can be formed, an extract phase containing solvent and dissolved aromatics and a raffinate phase. Suitable solvents are furfural, nitrobenzene, dimethyl formamide, liquid SO_2 and the like. Solvents are generally used at dosages of 100–600 percent, at temperatures between 120°–250° F., preferred conditions being dosages of 100–300 percent and temperatures between 120° and 180° F. A particularly suitable solvent is N-methyl pyrrolidone which can be used at a lower temperature and lower dosage than the other solvents mentioned above. In addition N-methyl 2-pyrrolidone is preferred because of its chemical stability and its ability to produce even lighter colored refined oils. The other solvents mentioned above also have a tendency to produce refined oils that are degraded and darkened in color.

To improve the pour point of the oil the raffinate recovered from the solvent refining is dewaxed. Dewaxing is generally effected by contacting the raffinate from the solvent extraction with a preferential solvent to separate waxy from nonwaxy material. Suitable solvents comprise a mixture of an aromatic hydrocarbon such as benzene, toluene or xylene with an alkyl ketone containing from three to eight carbon atoms such as acetone, methyl ethyl ketone, methyl propyl ketone and the like. Depending on the desired pour point and miscibility characteristics, the solvent may contain from about 40–60 percent ketone and 60–40 percent aromatic hydrocarbon. Dilution is generally in the range of 1.5–5 parts of solvent per part of oil. The mixture is chilled, filtered and washed, the filtering temperature being selected in accordance with the

desired pour point. Generally, the filtering is carried out at a temperature of from +20° F. to −30° F.

In the following example which is submitted for illustrative purposes only, oil 1 is a light distillate derived from a mixed base crude, oil 2 is also a light distillate derived from Louisiana crude, oil 3 is deasphalted residuum from West Texas Crude and oil 4 is derived from mixed base crude.

In each case, the hydrogenation catalyst contains 2.3 percent Ni and 10.0 percent Mo (as the oxide) supported on alumina, the solvent used in the solvent extraction step is N-methyl 2-pyrrolidone and that used in the dewaxing step is a mixture containing 50 percent methyl ethyl ketone and 50 percent toluene. Data for the treatment of the various oils appear in table I below.

TABLE I

	1		2		3		4	
	A	B	A	B	A	B	A	B
Hydrogenating conditions:								
Temperature, ° F		606		622		620		607
Pressure, p.s.i.g		500		500		560		500
Space velocity, v./hr./v		0.49		.50		.50		0.50
H_2, s.c.f./bbl		1,000		576		536		1,000
Tests:								
Gravity, ° API	23.9	26.2	28.0	29.2	25.1	25.3	20.7	23.4
Flash, COC, ° F	460	405	385	395	555	500	525	490
Viscosity, SUS at 210° F	56.6	52.5	42.7	42.1	123.5	108.4	132.1	115.8
Viscosity index	77.0	85.0	81.0	88.0	86.5	91.0	66.5	70.0
Carbon residue, percent	.23	.07	.03	.01	1.48	.97	1.60	1.27
Refractive index at 70° C	1.4868	1.4804	1.4718	1.4680	1.4870	1.4830	1.4970	1.4920
Solvent refining:								
Dosage, percent	120	110	220	200	300	275	180	120
Temperature, ° F	130	130	130	130	160	150	150	150
Yield, volume percent	73.8	78.2	65.2	70.6	70.7	76.2	68.7	76.9
Refined oil tests:								
Gravity, ° API	30.3	30.3	33.6	33.5	30.3	2.84	27.6	27.1
Flash, COC, °F	445	435	405	405	570	550		550
Viscosity, SUS at 210° F	51.0	50.6	41.2	41.2	105.6	100.0	84.1	90.9
Viscosity Index	105	99	109	111		102	96	95
Refractive Index	1.4633	1.4639	1.4533	1.4532	1.4695	1.4696	1.4714	1.4714
Solvent dewaxing:								
Dilution ratio	3:1	3:1	2.5:1	2.5:1	3:1	3:1	3:1	3:1
Wash ratio	2:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1
Temperature, ° F	0	0	−20	−20	−15	−15	0	0
Dewaxed oil tests:								
Viscosity, SUS at 210° F	55.6	55.2	43.3	43.6	102.2	105.6	107.6	105.6
Viscosity Index	89	90	96	103	95	96	78	82
Pour, ° F	+10	+10			−5	0	+5	+5

It can be seen from the foregoing that the mildly hydrogenated oils have higher API gravities, lower refractive indexes and higher VI's than the charge stocks. The mildly hydrogenated oils are also improved charge stocks for the solvent extraction resulting in yield increases of up to 10 percent when refining to the same quality level. This is true even when charge stocks containing more than 1 percent Conradson Carbon are used. In addition, the combination of mild hydrogenation followed by extraction using N-methyl pyrrolidone as the solvent results in finished products of good color.

Since the hydrogenation step is carried out at such a low-pressure, my process has advantages over prior art processes. In a specific embodiment of my invention, a crude oil is fractionated to produce a naptha, a lubricating oil stock is recovered from the heavier than naphtha fraction either by vacuum distillation or by deasphalting the residuum or both, the naphtha is catalytically reformed and effluent hydrogen without repressuring or purification is used for the mild hydrogenation of the lube oil stock. Advantageously, the reformer hydrogen can be used in the mild hydrogenation step on a once-through basis and returned to the reformer recycle stream.

Other modifications of the invention as hereinbefore set forth may be made without departing from the spirit and scope, thereof, and therefore, only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A method for refining a lubricating oil stock which consists of passing said lubricating oil stock into contact with a hydrogenation catalyst under mild hydrogenation conditions including a temperature between 575° and 800° F., and a pressure between about 250 and 600 p.s.i.g., to obtain a product liquid yield of substantially 100 percent, subjecting the resulting hyrogenation product to solvent extraction at a temperature between about 120° and 250° F. with a solvent having an affinity for aromatic hydrocarbons at a solvent to oil volume ratio of between 1:1 and 6:1 to produce an aromatic-rich extract and an aromatic-poor raffinate, and dewaxing the raffinate using as solvent a mixture comprising an alkyl ketone containing from three to eight carbon atoms and an aromatic hydrocarbon selected from the group consisting of benzene, toluene and xylene.

2. The process of claim 1 in which the hydrogenation catalyst comprises nickel and molybdenum.

3. The process of claim 1 in which the solvent having an affinity for aromatics comprises N-methyl pryrrolidone.

4. The process of claim 3 in which the temperature is between 120° and 180° F.

5. The process of claim 1 in which the dewaxing solvent comprises methyl ethyl ketone and toluene.

6. The process of claim 1 in which the hydrogenation temperature is not greater than 650° F. and the hydrogenation pressure does not exceed 500 p.s.i.g.

7. The process of claim 3 in which the lubricating oil stock contains at least 1 percent Conradson Carbon.

8. The process of claim 3 in which the solvent to oil volume ratio is between 1:1 and 3:1.

9. A process for the production of a lubricating oil which comprises fractionating a crude petroleum oil to recover a naphtha fraction therefrom, recovering a lubricating oil stock from the heavier than naphtha fraction, catalytically reforming the naphtha fraction, separating from the reformer effluent a hydrogen-rich stream, treating said lubricating oil stock in a process which consists of contacting same with a hydrogenation catalyst in the presence of at least a portion of said hydrogen-rich stream at a temperature between about 575° and 800° F. and a pressure between about 250 and 600 p.s.i.g, the pressure in the hydrogenation zone being substantially equal to the pressure in the catalytic reforming zone, subjecting the resulting hydrogenation product to solvent extraction at a temperature between about 120° and 250° F. with a solvent having an affinity for aromatic hydrocarbons at a solvent to oil volume ratio of between 1:1 and 6:1 to produce an aromatic-rich extract and an aromatic-poor raffinate, and dewaxing the raffinate using as solvent a mixture comprising an alkyl ketone containing from three to eight carbon atoms and an aromatic hydrocarbon selected from the group consisting of benzene, toluene and xylene.

10. The process of claim 9 in which the hydrogen-rich stream is passed through the hydrogenation zone on a once-through basis.